Ionic Conductivity in KC1-KBr Mixed Single Crystals

Technical Report 180
Laboratory for Insulation Research
Massachusetts Institute of Technology

May, 1963

The work reported in this document was made possible through support extended to the Massachusetts Institute of Technology, Laboratory for Insulation Research, by Air Force Cambridge Research Laboratories, Electronic Systems Division, under Contract AF 19(604)-8483. Reproduction of this report in whole or in part is permitted for any purpose of the United States Government.

Ionic Conductivity in KCl-KBr Mixed Single Crystals

by

Don Lee Cannon

Laboratory for Insulation Research
Massachusetts Institute of Technology
Cambridge, Massachusetts

Contract AF 19(604)-8483

May, 1963

IONIC CONDUCTIVITY IN KCl-KBr MIXED SINGLE CRYSTALS*

by

Don Lee Cannon†

Laboratory for Insulation Research
Massachusetts Institute of Technology
Cambridge, Massachusetts

Abstract: The ionic conductivity of KCl-KBr mixed single crystals as a function of the composition and thermal treatment of the samples has been studied. The intrinsic activation energy minimized at the composition 50/50 mole % KCl-KBr, while the intrinsic conductivity reached a maximum at 67/33 mole % KBr-KCl. Quenching increased extrinsic conductivity over that of annealed samples except in compositions near 50/50 mole % KCl-KBr, where it decreased extrinsic conductivity. It also slightly increased intrinsic conductivity in all compositions. These effects are explained in terms of structural defects and impurities.

Introduction

Most investigations on ionic conductivity have been made on alkali halides, since they are easily obtainable ionic compounds of relatively simple crystal structure. It is the purpose of this research to study the conductivities of the mixed KCl-KBr crystal system as a function of crystal composition and heat treatment.

---

*Based in part on a thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Electrical Engineering at Massachusetts Institute of Technology.

†Present address: Temco Electronics and Missiles Company, Dallas 22, Texas.

Foundations of Ionic Conductivity

Theory of Ionic Conductivity

In general, the conductivity can be expressed by

$$\sigma = n\mu q, \tag{1}$$

where n is the number of carriers per cm^3, q the charge of the carriers, and μ the mobility (in m/sec/volt/cm) of the carriers. The number of charge carriers and the mobility depend on temperature. Most workers consider mobility (which is related to the vibrational frequency of the lattice atoms) to be a constant, while a few have assumed a 1/T dependence. Since the number of carriers participating in conduction is an exponential function of temperature, either viewpoint is acceptable. The number of charge carriers participating in conduction is dependent on the total number of vacancies in the lattice at any given temperature and the number of these that move in the lattice. If N is the number of available structurally and thermally produced vacancies and ϵ the energy of vacancy motion, the number of vacancies participating in conduction is

$$n = N e^{-\epsilon/kT}, \tag{2}$$

where k is Boltzmann's constant and T the temperature ($^{\circ}$K). If n_i represents the structurally produced vacancies and $\phi/2$ the energy for thermal vacancy production, then the number of vacancies available at any given temperature is

$$N = n_i + n_o e^{-\phi/2kT}, \tag{3}$$

where n_o is the number of vacancies theoretically possible at $T = \infty$. Thus, considering μ a constant, Eqs. 1, 2, and 3 yield for the conductivity:

$$\begin{aligned} \sigma &= q\mu(n_i + n_o e^{-\phi/2kT})e^{-\epsilon/kT}, \\ \sigma &= n_i\mu q e^{-\epsilon/kT} + n_o\mu q e^{-(\phi/2+\epsilon)/kT}. \end{aligned} \tag{4}$$

The exponents are known as activation energies, usually expressed in electron volts. If more than one ion participates in conduction, there is an expression similar to Eq. 4 for each such ion. The total conductivity is the sum of the individual conductivities. In the KCl-KBr system, conduction is predominantly cationic; the above simple expression therefore suffices.

Ionic conductivity thus takes place by the jumping of ions into vacancies (Schottky defects); the number of such jumps is proportional to n. If n_i (impurity-produced and frozen-in defects) $\gg n_o e^{-\phi/2kT}$ for certain temperatures, one has conduction whose activation energy is a low ϵ and whose magnitude depends on the history and impurity content of the crystal. This is the structure-sensitive or extrinsic region of conductivity. If the temperatures are high enough so that $n_o e^{-\phi/2kT} \gg n_i$, then there is a conduction characterized by a high activation energy of $\phi/2+\epsilon$ and a much larger pre-exponential factor than in the extrinsic case. Conductivity in this range is dependent only on the energy required to produce vacancies, a reproducible property of the crystal, and is thus termed the intrinsic region of conductivity.

Both of these conductivity regions will generally be observed. If $n_o e^{-\phi/2kT} \gg n_i$ (as in a very pure or very nearly perfect crystal) for all temperatures of interest, only the intrinsic region is noted. It is possible to observe more than two regions, if there is interaction between impurities and vacancies or between vacancies and other vacancies or if one has precipitation of impurity halide phases within the lattice. When such additional regions occur, they usually appear at temperatures between those of the intrinsic and extrinsic regions or just below those of the extrinsic region.

For a more detailed theoretical presentation, see, for example, Lidiard's article,[1] which surveys the theoretical and experimental state of ionic conductivity up to 1957.

Experimental History of Ionic Conductivity

Plotting log σ versus $1/T$ generally yields two intersecting straight lines with different slopes, from which one can compute the activation energies. The intersection of these lines with $1/T = 0$ indicates the pre-exponential factors

$$\sigma_{oi} = n_o \mu q; \; \sigma_{oe} = n_i \mu q. \tag{5}$$

It is the variation of the activation energies and pre-exponential factors that concern experimental investigations of ionic conductivity.

Lehfeldt,[2] and Phipps and Partridge[3] investigated conductivities of several alkali halides, including KBr and KCl, while Kelting and Witt[4] established the effect of divalent impurities on conductivity. Later work has mainly verified these early investigations, though some disagreements have been found in KBr. The more important published data are summarized in Table 1.[1-13]

1) A. B. Lidiard, "Handbuch der Physik," Vol. 20, Springer-Verlag, Berlin, 1957, p. 248.

2) W. Lehfeldt, Z. Physik 85, 717 (1933).

3) T. E. Phipps and E. G. Partridge, J. Am. Chem. Soc. 51, 1331 (1929).

4) H. Kelting and H. Witt, Z. Physik 26, 197 (1949).

5) C. Wagner and P. Hantleman, J. Chem. Phys. 18, 72 (1950).

6) C. G. Brennicke, J. Appl. Phys. 11, 202 (1940).

7) V. Klemas, S. M. Thesis, M. I. T., 1959.

8) H. Kanzaki, K. Kido, and T. Ninomiya, J. Appl. Phys. 33, 482 (1962).

9) H. Gründig, Z. Physik 158, 577 (1960).

10) B. S. H. Royce and R. Smoluchowski, Phys. Rev. 122, 1125 (1961).

11) C. Ballard, ibid. 123, 744 (1961).

12) C. Tubandt, "Handbuch der Experimentalphysik," Vol. 12, Pt. 1, Akademische Verlagsgesellschaft, Leipzig, 1932, Chap. 3, p. 384.

13) W. Jost and H. Schweitzer, Z. phys. Chem. B20, 118 (1933).

Table 1. Survey of published results on conductivity.

Parameter	KCl	Ref.	KBr	Ref.
Intrinsic activation energy (ev)	2.06	2	1.97	2
	2.02	3	1.97	3
	1.96	5	1.88±0.1	7
	1.99	6		
Extrinsic activation energy (ev)	0.99	3	0.97	3
	0.83	8	1.06	6
	1.40	8	0.88±0.05	7
	0.77±0.02	9	0.65±0.02	9
	1.00±0.05	10		
	0.84-0.86	11		
Intrinsic pre-exponential factor (10^6 ohm^{-1} - cm^{-1})	2.00	2	1.5	2
	1-1.5	3	1-1.3	3
	0.55	5	1-4	7
	1-50	6		
Conductivity at melting point (10^{-4} ohm^{-1} - cm^{-1})	2.0	2	2.0	2
	1.9	5	1.5	3
Transport number t_+	0.88 - 0.96 (for T=435° to T=600°C)	12	0.5 (for T=605°C)	13

It will be seen that in KCl and KBr the transport is essentially cationic, though Jost and Schweitzer's[13] study on KBr indicates a significant anionic transport. However, their findings are in doubt as they indicate high cationic transport in KI which in view of the known high cationic transport in KCl would seem to discredit the possibility of lower cationic transport in KBr.

While in general there are two conductivity regions, only one has been observed in thallium halides.[3)] Dreyfus and Nowick[14,15)] observed up to five separate regions of ionic conductivity in NaCl and KCl; an activation energy of about 1.00 ev was determined for a straight-line transition region occurring between the intrinsic and extrinsic regions. Even horizontal transition regions have been observed, notably by Phipps and Partridge[3] and by Shapiro and Kolthoff.[16)] Hevesy[17)] (cf. Ref. 1) conducted an early study concerning the thermodynamic aspects of the mixed KCl-KBr single-crystal system. Smakula, Maynard, and Repucci[18)] studied its defect densities, microhardness, lattice constant, and ultraviolet absorption edge versus composition. The only previous study of ionic conductivity in the KCl-KBr system was done by Schultz.[19)] The variation of conductivity at 645°C with composition indicated maximum conductivity at 67/33 mole % KBr-KCl (about 3.3×10^{-6} ohm^{-1} - cm^{-1}) with KCl showing a value of about 1.6 and KBr one of about 2.8×10^{-6} ohm^{-1} - cm^{-1}. Of other mixed crystals, only TlCl-TlBr has been studied;[20)] here the extrinsic activation energies were somewhat higher in the mixed system than in the pure components, while the intrinsic properties were not affected by composition.

There is still a need for further work on the ionic conductivity of KBr and mixed crystals. Of the several studies made on KBr, the investigations

---

14) R.W. Dreyfus and A.S. Nowick, Phys. Rev. 126, 1366 (1962).

15) R.W. Dreyfus and A.S. Nowick, J. Appl. Phys. 33, 473 (1962).

16) I. Shapiro and I.M. Kolthoff, J. Chem. Phys. 15, 41 (1947).

17) G. v. Hevesy, "Handbuch der Physik," Vol. 8, Springer-Verlag, Berlin, 1928, p. 263.

18) A. Smakula, N.C. Maynard, and A. Repucci, J. Appl. Phys., Suppl., 33, 453 (1962).

19) H. Schultz, Thesis, University of Göttingen, 1952.

20) B. Leibenhaut, S.B. Thesis, M.I.T., 1959.

of Lehfeldt,[2] and Phipps and Partridge[3] will be referred to later.

Experimental Procedures

Measurement Techniques

The conductivity of the samples was measured using General Radio 713B and 805A oscillators for generating the 1-, 10-, and 100-kc voltages that were applied. Actual measurement was made with a modified General Radio 716A bridge and a sensitive detector circuit. This equipment, normally used for conductivity and dielectric-constant measurements, was used previously by Klemas,[7] but was modified for increased sensitivity.

Sample Holders

A good sample holder must provide low loss, low noise, and uniform and constant temperature. The electrical requirements are usually easily met, but control of temperature may prove difficult. The main problem is to prevent a temperature gradient from developing across the sample. Such a gradient causes an uncertainty in the sample temperature and thus can produce large errors in the determination of activation energies. A gradient of 2 or 3% affects the activation energy by about 2%. The occurrence of a constant gradient of 15°C over the entire intrinsic range from 400° to 650°C will cause an increase in activation energy of 0.15 to 0.18 ev, corresponding to a 10% error. Gradient measurements were made on two holders used; the older one, used by Klemas,[7] was found to have an acceptable $2\frac{1}{2}$ % gradient between 100° and 700°C. In the new multiple-sample holder, which exhibited an acceptable gradient of 3% between 50° and 350°C, the gradient from 400° to 650°C was 15°C, making the holder useless for intrinsic range measurements. As a result, all runs that included both intrinsic and extrinsic temperatures had to be made in the older single-sample holder, while certain extrinsic studies were made in the new, multiple-sample holder.

Sample Preparation

The crystals used were cleaved into samples of 0.2 to 0.3 cm thickness and from 0.5 to 1.5 cm on a side and then ground flat to within approximately 2.10^{-4} cm. The side surfaces were polished to minimize surface conduction effects at the lower temperatures. Colloidal graphite (alcoholic solution) electrodes were applied to the large surfaces, and gold leaf electrodes, cut to the size of the sample, were pressed onto the graphite electrodes to insure uniform electrical contact with the holder electrodes. The colloidal graphite was not ideal as a base electrode because of its tendency to oxidize in the presence of air and to flake off at high temperatures. To minimize these effects it was necessary to apply the electrodes carefully and to provide an oxygen-free atmosphere at the high temperatures.

The samples were also subjected to thermal treatment, such as quenching and annealing, prior to measurement. For all compositions, two identical samples were heated at about 650°C for 24 hours, and then one was rapidly quenched to room temperature, while the other was annealed by bringing it to room temperature at 50°C per hour. At least two sets of such twin samples were taken from separate crystals for each composition. Despite the tendency of the mixed crystals to shatter, at least two separate sets of identical samples were obtained in the unprocessed, annealed, and quenched conditions for all compositions.

Table 2A. Effect of composition on intrinsic conductivity.

		KCl	67/33 mole % KCl-KBr	50/50 mole % KCl-KBr	33/67 mole % KCl-KBr	KBr
Intrinsic activation energy ϵ (ev)	All runs	1.88-1.98	1.82-1.88	1.72-1.76	1.78-1.83	1.56-1.65, 1.91
	Average	1.92 ± 0.03	1.84 ± 0.03	1.74 ± 0.02	1.81 ± 0.02	1.62 ± 0.033, 1.91
	Ref. 2					1.97
	Ref. 3	2.02	-	-	-	-
Vacancy production energy $\phi/2$ (ev)	All runs	1.17-1.28	1.10-1.22	1.03-1.18	1.16-1.20	0.78-1.08, 1.26
	Average	1.23 ± 0.07	1.17 ± 0.07	1.08 ± 0.08	1.198 ± 0.03	0.922 ± 0.11, 1.26
Intrinsic pre-exponential factor $\sigma_{oi} \times 10^{-5}(ohm^{-1}cm^{-1})$	All runs	1.78-11.2	2.14-5.62	0.162-2.4	1.82-4.57	0.0246-0.162, 10
	Mean	4.46	3.47	0.59	2.88	0.0632, 10
	Ref. 2	-	-	-	-	20
	Ref. 3	20	-	-	-	-
Intrinsic conductivity (T = 575°C) $\sigma_i \times 10^{6}(ohm^{-1}cm^{-1})$	All runs	0.38-2.24	0.83-6.03	1.41-3.8	3.8-6.8	0.933-2.51
	Mean	1.0	2.18	3.16	3.9	1.48
	Ref. 19	1.6	-	-	3.3	2.8
Number of intrinsic runs		8	8	12	7	11

All deviations are standard deviations; "mean" denotes geometrical mean.

Table 2B. Effect of composition on extrinsic conductivity.

		KCl	67/33 mole % KCl-KBr	50/50 mole % KCl-KBr	33/67 mole % KCl-KBr	KBr
Extrinsic activation energy ϵ (ev)	All runs	0.53-0.76	0.62-0.72	0.55-0.72	0.59-0.64	0.51-0.87, 0.65
	Average	0.7 ± 0.06	0.67 ± 0.03	0.65 ± 0.05	0.612 ± 0.02	0.69 ± 0.12
Extrinisc pre-exponential factor $\sigma_{oe} x10^4 (ohm^{-1} cm^{-1})$	All runs	0.34-57.5	4.16-58.9	0.76-87.1	0.55-5.89	0.126-68.2
Extrinsic conductivity (T = 253°C) $\sigma_e x10^{10} (ohm^{-1} cm^{-1})$	All runs	0.48-6.16	4.5-10.5	0.102-8.7	2.18-4.07	0.68-22.9
	Mean	2.48	6.84	3.7	2.88	2.35
Transition conductivity (T = 400°C) $\sigma_t x10^8 (ohm^{-1} cm^{-1})$	-	0.2	1.5	0.85	0.83	0.56
Number of extrinsic runs		14	8	12	6	21

Experimental Results

The Effect of Composition on Conductivity

To study the variation of conductivity with composition, samples of 100 mole % KCl, 67/33 mole % KCl-KBr, 50/50 mole % KCl-KBr, 33/67 mole % KCl-KBr, and 100% KBr (all in mole %) were investigated, and their activation energies and pre-exponential factors were computed. Condensed results are summarized and shown to be in general agreement with those of other workers (Table 2). The KBr samples yielded intrinsic activation energies in wide disagreement with the literature and with reasonable extrapolation of other data in this research. While the intrinsic activation energy of KCl of 1.92 ev agrees well with accepted values, the majority of 11 runs on KBr yielded a consistent low 1.62 ± 0.03 ev activation energy. More recent measurements on pure, zone-refined KBr has given 1.91 ev, which appears more reasonable. The reason for the discrepancy in KBr will be discussed later; the more acceptable value of 1.91 ev has been used in the appropriate plots.

Typical plots of $\ln \sigma$ versus $1/T$ in KCl and in 50/50 mole % KCl-KBr are given in Fig. 1. Figure 2 shows the same data for KCl plotted as $\log (T\sigma)$ versus $1/T$, as would be the case if μ had a $1/T$ dependence. Only 16 of the 47 complete plots obtained in this research exhibited a marked transition region, and in none of these was any multiple-region behavior observed, as found by Nowick and others.[10,14,15] The transition regions that did occur did not really exhibit definite straight-line portions except in one KBr and one 50/50 mole % KBr-KCl plot. Some of the plots showed a horizontal transition region, indicating saturation of extrinsic vacancies.

In Fig. 3 a plot of intrinsic activation versus composition shows that

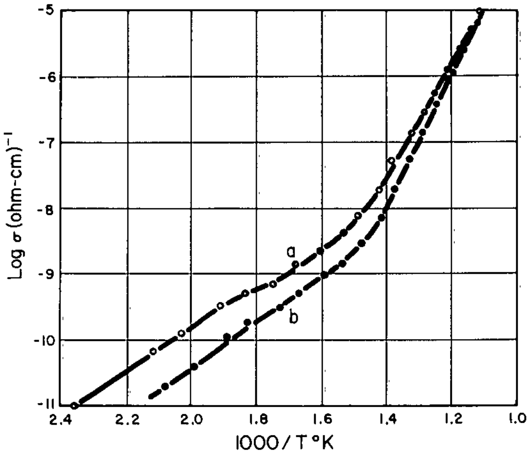

Fig. 1. Conductivity of (a) KCl and (b) 50/50 mole % KCl-KBr crystals versus 1/T.

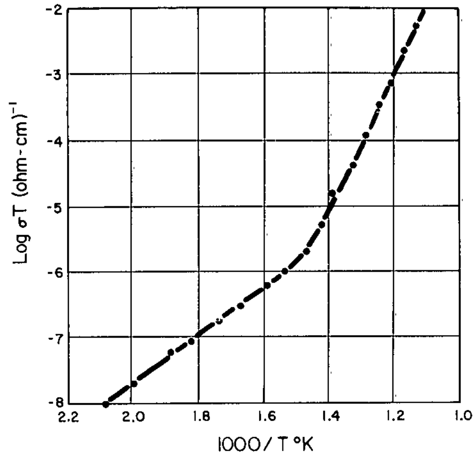

Fig. 2. Conductivity of KCl crystal versus 1/T.

with a value of 1.91 ev for KBr one gets an almost symmetrical plot, exhibiting a minimum at 50/50 mole % KCl-KBr. The value of 1.62 ev completely destroys the symmetry, indicating that whatever causes this unusual slope is not inherent in the other members of the system. Also plotted in Fig. 3 are the extrinsic activation energy and the vacancy-pair production energy $\phi/2$ (see Eq. 4) versus composition. It is obvious that the ϕ component of the over-all intrinsic activation energy is the parameter responsible for the low 1.62 ev for KBr. The extrinsic activation energy seems to minimize at 67/33 mole % KBr-KCl, even though the spread of the data makes a definite statement impossible. The pre-exponential factors were not plotted because the intrinsic pre-exponential factor

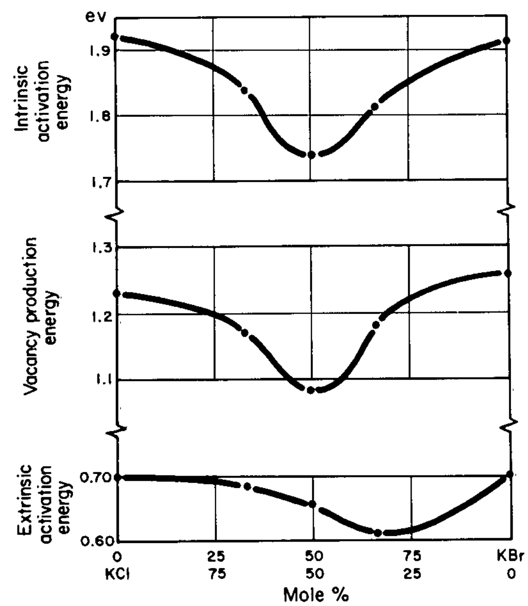

Fig. 3. Activation energy of KCl-KBr mixed crystals vs. composition.

behaves exactly like ϕ and intrinsic activation energy, while the extrinsic pre-exponential factor is not defined well enough for plotting.

In Fig. 4 the magnitudes of the extrinsic, transition, and intrinsic conductivities are plotted versus composition at arbitrarily chosen temperatures of 253°, 400°, and 575°C, respectively. The intrinsic conductivity maximizes at 67/33 mole % KBr-KCl in agreement with Schultz.[19] The extrinsic and transition conductivities are essentially constant except for a small peak near 67/33 mole % KCl-KBr.

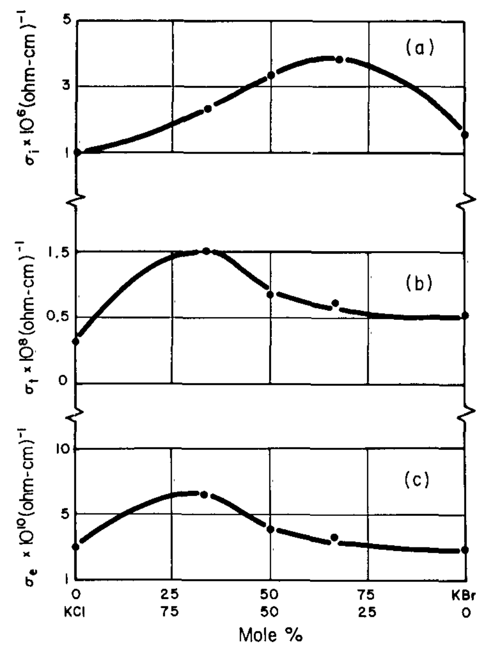

Fig. 4. Conductivity of KCl-KBr mixed crystals vs. composition; (a) intrinsic, 575°C; (b) transition, 400°C; (c) extrinsic, 253°C.

Effect of Thermal Processing on Conductivity

The effect of thermal processing on the conductivity of the various compositions is summerized in Table 3. To determine the relative magnitudes of various quantities, ratios of the appropriate quantities have been computed. Thus, σ_A/σ_Q refers to the ratio of annealed to quenched conductivities, and $\epsilon N/\epsilon Q$ to that of the unprocessed-sample extrinsic to the quenched-sample activation energy. Intrinsic activation energies and pre-exponential factors are not listed because they were not affected by the thermal processing, as expected, since thermal treatment normally influences only the extrinsic region. An exception is illustrated by the fact that both σ_A/σ_Q and σ_N/σ_Q evaluated at 575°C are less than unity, indicating that quenching consistently

Table 3. Effect of heat treatment on conductivity.

	KCl	67/33 mole % KCl/KBr	50/50 mole % KCl-KBr	33/67 mole % KCl-KBr	KBr
σ_A/σ_Q, T=575°C	0.815	0.815 0.792	0.66 0.66	0.707 0.869	0.74, 0.873
σ_N/σ_Q, T=575°C		0.935 0.812	0.775 0.66	0.66 0.776	0.76
σ_A/σ_Q, T=253°C	0.407, 0.603 0.738	1.12 0.725	1.41, 4.9 3.64	1.1 0.975	0.706, 0.645 1.7, 0.81, 0.76
σ_N/σ_Q, T=253°C	2.4 2.09	2.36 1.71	3.46 5.92	1.87 1.58	0.373, 1.7 0.295, 0.204
ϵ_A/ϵ_Q	1.25, 1.008 0.97	1.05 1.048	0.94, 0.94 0.912	0.984 0.965	0.95, 0.994 1.17, 0.774, 0.99, 1.03
ϵ_N/ϵ_Q	1.033 1.019	1.15 1.082	0.888 1.019	1.031 1.041	1.205, 0.852 1.288, 1.17

These quantities are the ratios of annealed or unprocessed intrinsic conductivities σ and extrinsic conductivities σ and activation energies ϵ to their quenched values. If the ratio is less than 1, quenching increased the parameter over that of its annealed or unprocessed value. If the ratio is greater than 1, the reverse is true.

increased the intrinsic magnitudes over that of the unprocessed and annealed samples (Fig. 5).

The effect of thermal processing on the extrinsic conductivity of the various compositions is presented in Fig. 6. Except in KBr, the conductivities were always less in quenched than in unprocessed samples in the extrinsic region; in the case of 50/50 mole % KCl-KBr this effect is especially pronounced. It is seen that for compositions between 67/33 mole % KCl-KBr and 67/33 mole %

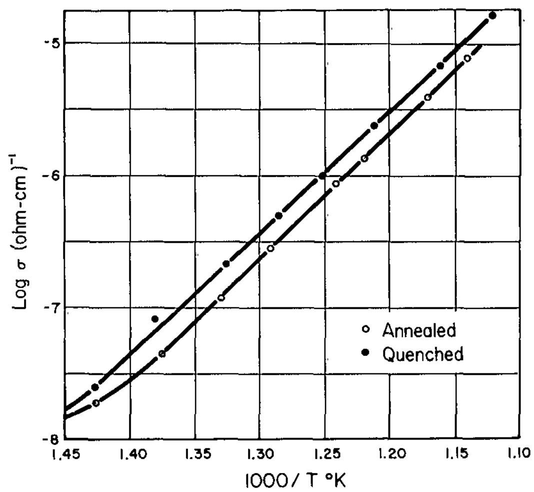

Fig. 5.

Effect of heat treatment on intrinsic conductivity of 67/33 mole % KCl-KBr crystal.

KBr-KCl quenching brought the conductivities below those of the annealed samples ($\sigma_A/\sigma_Q > 1$), while for the other compositions it increased the conductivities above those of the annealed samples ($\sigma_A/\sigma_Q < 1$). This behavior is summarized in Fig. 7, which illustrates its symmetry. Table 3 shows that in the case of 50/50 mole % KCl-KBr quenching lowered the conductivity significantly below that of the annealed and unprocessed samples ($\sigma_A/\sigma_Q \gg 1$), and also that from the ϵ_A/ϵ_Q and ϵ_N/ϵ_Q entries, that heat treatment had but little effect on the extrinsic activation energies.

Other Results

The magnitudes of the extrinsic ranges, as well as the temperature and conductivity at the intersection of the extrinsic and intrinsic lines, give an indication of the divalent impurity concentration. Thus a comparison of these parameters in carefully annealed samples gives a very rough idea of the positive divalent impurity content of the sample. A scrutiny of the extrinsic conductivities indicates that all compositions in this work have about the same purity (see Fig. 8); and comparison with plots of other workers seems to indicate that our

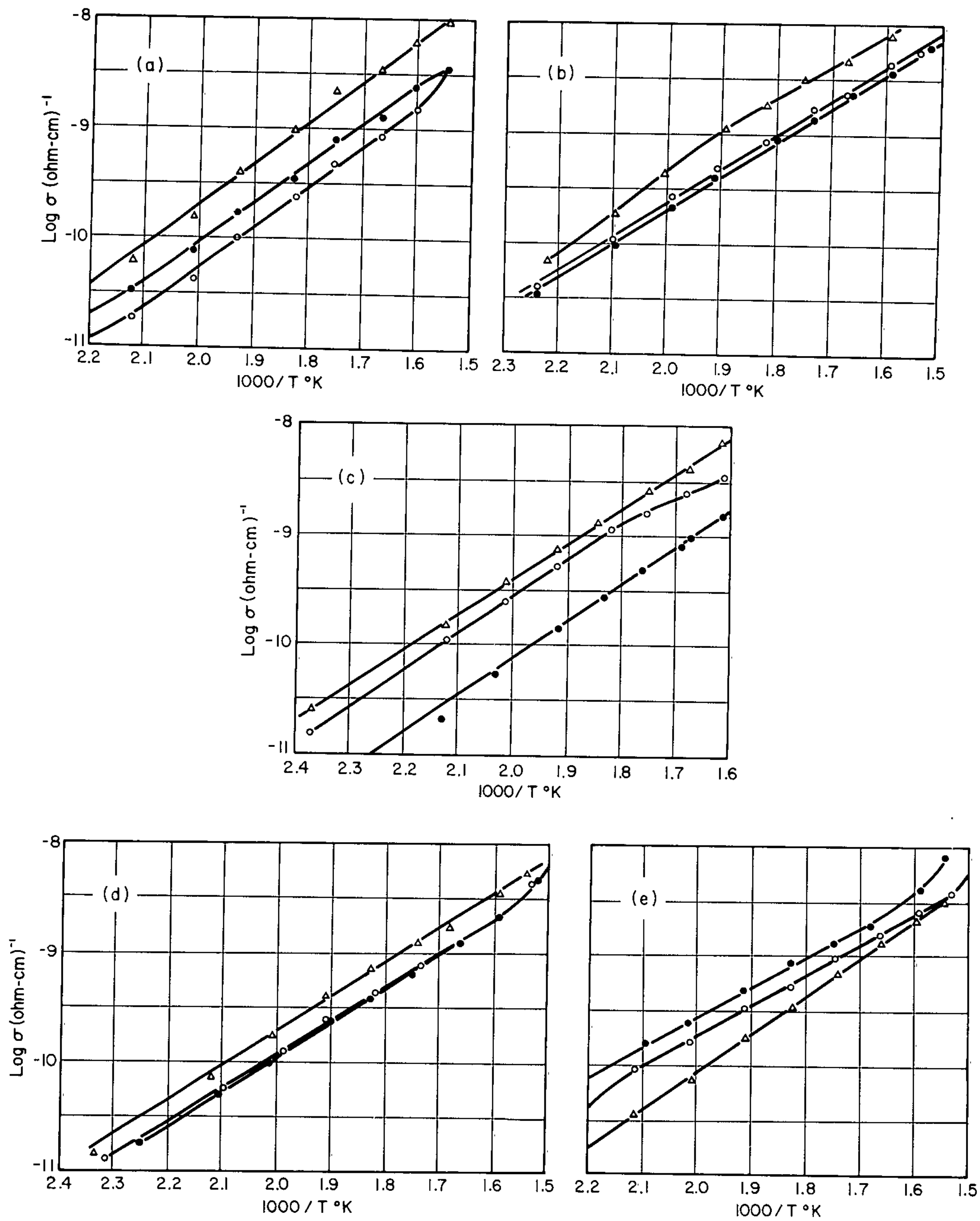

Fig. 6. Effect of heat treatment on extrinsic conductivity of (a) KCl, (b) 67/33 mole % KCl-KBr, (c) 50/50 mole % KCl-KBr, (d) 33/67 mole % KCl-KBr, (e) KBr crystal; Δ unprocessed, o annealed, ● quenched sample.

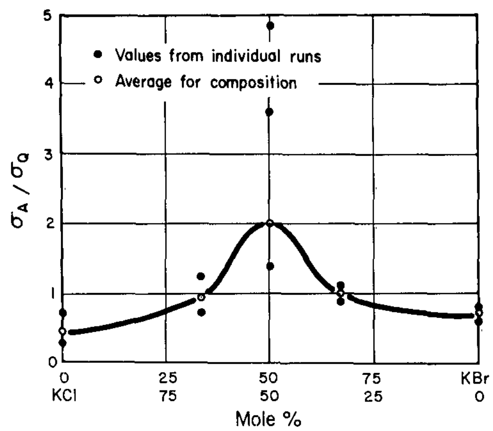

Fig. 7. Effect of heat treatment on extrinsic conductivity vs. composition of KCl-KBr mixed crystals.

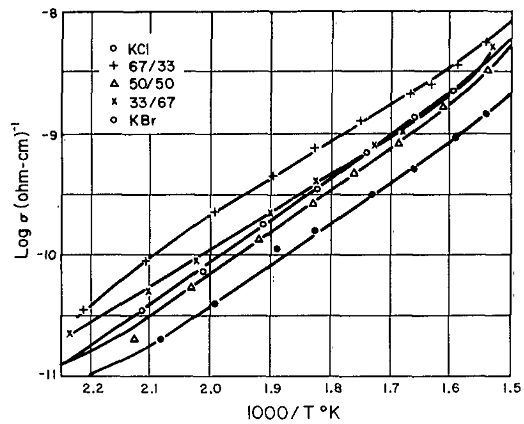

Fig. 8. Extrinsic conductivity of KCl-KBr of various composition.

samples are equivalent to those used by others. The relationship between 1/T and ln σ at the transition region suggests that KBr and 67/33 mole % KBr-KCl were somewhat purer than the other compositions. The plots that show horizontal transition regions give a direct indication of the purity, and samples of KBr and KCl which exhibited such regions show no significant difference in impurity. The results of a spectrophotometric analysis on KCl and KBr samples* are given in Table 4. The excess of Ba^{2+} in KCl and Na^{+} in KBr is evident.

Another extrinsic phenomenon became apparent during measurement of the KBr crystals. In all runs, data were taken while increasing the temperature from 50° to 650°C. On some runs, immediately after finishing this temperature run, data were taken while decreasing the temperature back to 50°C. In the case of KCl the data for increasing and decreasing temperatures agreed very closely. In the case of KBr, however, the extrinsic data for increasing temperature differed significantly from those for decreasing temperature, whereas the intrinsic region was not changed. A typical set of data for KBr is shown in

* Made by J. Hwang of the Crystal Growth Group of this laboratory.

Table 4. Spectrographic analysis of impurities in KCl and KBr crystals.

Samples	Impurity-element concentration							
	Ba	Ca	Cu	Mg	Na	Al	Si	Pb
KCl	0.001	0.002	0.002	0.002	0.020	0.0005	0.001	0.001
KBr	0.002	0.002	0.003	0.002	0.010	0.0005	0.001	0.001
Concentrations are approximate and in wt. %.								

Table 5. Comparison of intrinsic activation energies of log σ versus 1/T and log (σT) versus 1/T plots.

Activation energy (ev)	Composition				
	KCl	67/33 mole % KCl-KBr	50/50 mole % KCl-KBr	33/67 mole % KCl-KBr	KBr
From log σ versus 1/T plot	1.92	1.84	1.74	1.81	1.62 1.91
From log (σT) vs. 1/T plot	2.05	1.92	1.86	1.92	1.74 2.04

Fig. 9. The magnitude and slope of the extrinsic region taken while decreasing temperature was reproducible and independent of both the applied field frequency and field strength and of whether the run was made under vacuum or nitrogen.

Several workers[10, 14, 15, 21] have found an inverse temperature in the mobility factor, so that instead of plotting log versus 1/T, one should really plot log (Tσ) versus 1/T in order to examine the conductivity properly. Some of the data plotted in this way are shown in Fig. 1 (p. 12). Important conductivity parameters are listed in Table 5 (cf. Table 2); not all data were

21) N. F. Mott and R. W. Gurney, "Electronic Processes in Ionic Crystals," 2nd ed., Oxford University Press, London, 1950.

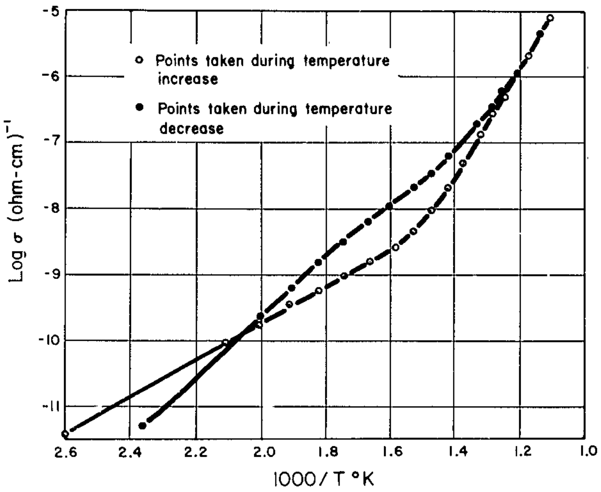

Fig. 9.

Irreversibility of extrinsic conductivity in KBr.

processed in this way. One can see from Fig. 2 that the curves are essentially the same as that of log σ versus 1/T shown in Fig. 1. Close and expanded-scale studies indicate that both plots have the same deviations and reliability and are thus equally accurate. While the log $T\sigma$ plots have higher activation energies (6% or about 0.1 ev) than the corresponding log σ energies, their behavior with composition and thermal processing is generally the same. Since the intrinsic activation energies in the log σ plot are within experimental error, the log $T\sigma$ plots cannot improve on this. Thus it is impossible to say whether the mobility factor has a 1/T dependence.

Expanded-scale plots of all five compositions have been made for both the extrinsic and intrinsic regions in Figs. 8 and 10, respectively.

Discussion

Lidiard[1)] pointed out that the reason for the paucity of work done on mixed crystals is that such conductivity measurements seemed to offer little additional information. Data obtained in this research, on the other hand, show that the changes in the parameters with composition and heat treatment are

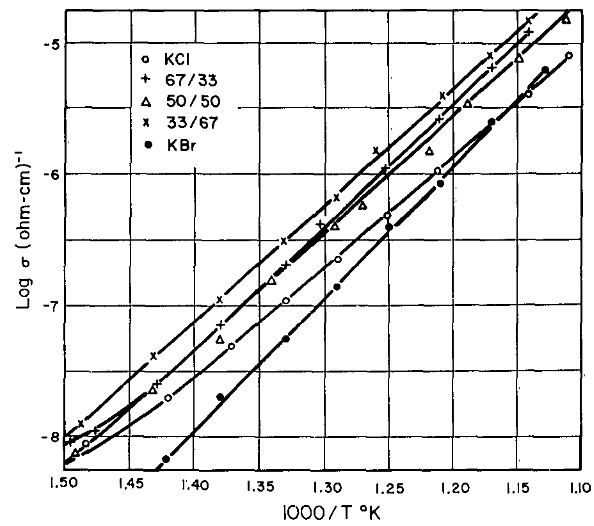

Fig. 10.

Intrinsic conductivity of KCl-KBr of various composition.

neither trivial nor easily understood. To understand the effects observed, one must try to correlate the changes in composition and thermal history to various factors in the relations for ϕ, etc., or else reason from structural considerations with minimum reference to theoretical relationships. The latter procedure is chosen for this discussion. The important factors in ionic conductivity are the number of carriers available at any given temperature and the ease with which these carriers can move in the lattice. In the extrinsic region the motion of vacancies produced by impurities, various defects, or frozen-in vacancies is significant while in the intrinsic region it is the number of thermally produced vacancies and their motion. All of these are closely related to the lattice structure. Thus, changes in the distribution of non-identical ions within the lattice should lead to changes in conductance.

Effect of Composition

The behavior of the intrinsic activation energy is due primarily to the vacancy production energy ϕ(cf. Fig. 3). In a perfectly symmetrical electric field, an ion is in a very stable configuration and is difficult to remove. As one changes the composition from either pure component to 75/25 mole % KCl-KBr or 25/75 mole % KCl-KBr, the symmetry decreases and the electrical forces operating on the K^+ ion become less effective. Here it is easier to remove the cation from its lattice site than in either of the pure components. Furthermore, either mixed composition will behave the same, since the symmetry depends essentially on the ratio of the number of one to that of the other anion. The greatest electric-field distortion is near the 50/50 mole % KCl-KBr composition which exhibits the lowest activation energy.

The extrinsic activation energy reached its minimum at 67/33 mole % KBr-KCl, the same composition at which the intrinsic conductivity maximized. The reason these two parameters reach extrema at this composition is probably related to the fact that the melting point also reaches a minimum here. The fact that $\phi/2$ minimized at 50/50 mole % KCl-KBr indicates that thermal production of vacancies has little relation to the effects considered here. Thus, the data tend to indicate that either the vibrational frequency of ions is greater (at a given temperature) or that the motion of vacancies requires less energy at the composition 67/33 mole % KBr-KCl. Both effects cause the maximum in intrinsic conductivity while the former also supports the minimum of the system melting point.

Effect of Heat Treatment

The effect of heat treatment on the magnitude of extrinsic conductivity is given in Figs. 6 and 7. Generally, such treatment tends to freeze in the vacancies produced at high temperatures. In the case of pure KCl and KBr, quenching freezes in many of the thermally produced vacancies while annealing causes the freezing in of a smaller number of such vacancies. Thus, in pure KCl and KBr the extrinsic conductivity in quenched crystals is higher than in annealed ones. In mixed crystals the number of frozen-in vacancies depends not only on the rate at which temperature is lowered, but also on the anion distribution. At high temperatures the anion distribution is random; in quenched crystals this randomness remains, while in annealed crystals some preferential redistribution may take place, depending on the composition or on the ratio of Cl^- and Br^- ions. The randomness of the anion distribution apparently controls the number of vacancies frozen in the lattice. In 50/50 mole % KCl-KBr, where quenching significantly lowers the conductivity below that of the annealed samples, the random anion distribution at high temperatures seems to act so as to leave a smaller number of vacancies upon quenching and a relatively high number upon annealing. In 67/33 mole % KCl-KBr or 67/33 mole % KBr-KCl this effect leaves the same number of vacancies in quenched and annealed samples.

Another effect of heat treatment observed in the intrinsic conductivity is illustrated by Fig. 5. Quenching increased the intrinsic conductivity above that of the annealed samples for all compositions. Since the intrinsic activation energies remained unaffected, this phenomenon must be due to a change in the intrinsic pre-exponential factor:[21)]

$$\sigma_{oi} = \frac{Ne^2a^2}{kT}\,\nu\left(\frac{\nu}{\nu'}\right)^{3z} \exp\left[-\frac{\alpha V_o}{k}\left(\frac{U_o}{V} + \frac{W_s}{V}\right)\right], \qquad (6)$$

where N is the number of atoms in lattice, a the lattice parameter, e the electronic charge, ν the vibrational frequency of atom in perfect lattice, ν' the vibrational frequency of atom near vacancy, z the number of atoms surrounding vibrational site, α the coefficient of thermal expansion, V_o the lattice volume at $T = 0^oK$, V the lattice volume, U_o the barrier energy at $T = 0^oK$, W_s the lattice energy. Since this effect was the same for all compositions, it cannot be due to the number of vacancies created by quenching, for otherwise the behavior would be as found in the extrinsic conductivities. This eliminates the term $(\nu/\nu')^{3z}$, the ratio of the vibrational frequency of an atom in a perfect lattice to that of an atom near a vacancy, raised to a factor depending on the number of counterions in the unit cell. Also, the lattice constant and the volume at 0^oK would not be expected to be changed by quenching, nor would the vibrational frequency ν or the thermal expansion parameter α. The only remaining possibilities are that the derivatives with respect to volume of either W_s or U_o (as evaluated at 0^oK) decrease. The latter is essentially the extrinsic activation energy; since the data do not indicate any consistent decrease with quenching, it is probably not responsible. Thus, one must either appeal to a decrease in $\partial W_s/\partial V$ or assume that quenching produces dislocations or other structural faults that add to the conductivity. Further experimental work needs to be done to determine which, if either, of these explanations is correct.

Discrepancies in the KBr Data

The KBr data, especially the low intrinsic activation energies, are at variance with both work done by others and with the investigations made on zone-refined KBr in this research, perhaps because of the presence of the Na^+ impurity. The analyses of KBr and KCl of Table 4 (p. 18) indicate two impurities, Na^+ and Ba^{2+}, present in quantities large enough to cause noticeable change in intrinsic properties. The Ba^{2+} ion has a radius very similar to that of the K^+ ion; thus, while its incorporation into the lattice would cause a large number of cation vacancies and enhance extrinsic conductivity, it can easily be incorporated substitutionally in the K^+ position, causing no change in ϕ. The Na^+ must therefore be the perturbing impurity. Apparently, the Na^+ is incorporated in a nondistorting way into the KCl and other composition crystals, so that it probably occupies normal cationic positions. This impurity could also account for the behavior noted in Fig. 9.

Acknowledgment

The author wishes to thank Professor A. Smakula for guidance throughout this work; Mr. A. Repucci for supplying the crystals, and Mr. W. B. Westphal for valuable discussions.

ductivity, it can easily be incorporated substitutionally in the K^+ position, causing no change in ϕ. The Na^+ must therefore be the perturbing impurity. Apparently, the Na^+ is incorporated in a nondistorting way into the KCl and other composition crystals, so that it probably occupies normal cationic positions. This impurity could also account for the behavior noted in Fig. 9.

Acknowledgment

The author wishes to thank Professor A. Smakula for guidance throughout this work; Mr. A. Repucci for supplying the crystals, and Mr. W. B. Westphal for valuable discussions.